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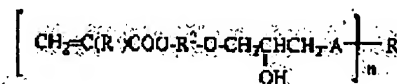
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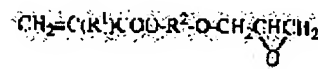
(54) (METH)ACRYLATE DERIVATIVE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a new compound obtained from a glycidylalkyl (meth) acrylate having a specific structure, excellent in adhesion to a substrate, and having flexibility and also low viscosity.



SOLUTION: This new compound is represented by formula I (R¹ is H or methyl; R² is a 4-10C alkylene; A is OOC, O or the like; R³ is a residual group after an active hydrogen-containing functional group is eliminated from a compound having the active hydrogen-containing functional group; n is 1 to 4). The compound of formula I is obtained by reacting a compound of formula II (e.g. 4-hydroxybutyl acrylate glycidyl ether or the like) with a compound of the formula X_n-R³ (X is carboxy, OH or the like), e.g. phthalic acid or the like. The above reaction is preferably carried out at 100-150°C for 2-5 h in an inert solvent (e.g. toluene) in the presence of a catalyst (e.g. triethylamine).



LEGAL STATUS

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

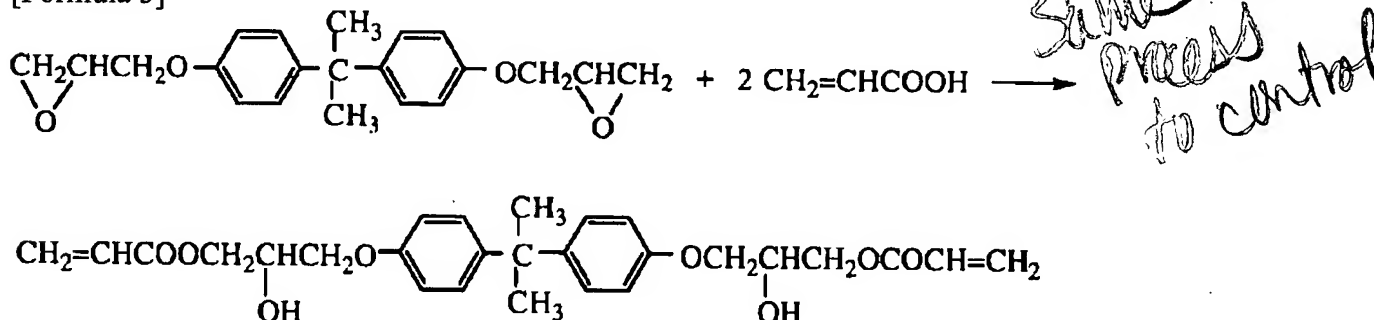
[Field of the Invention] This invention relates to an acrylate (meta) derivative and its manufacture approach.

[0002]

[Description of the Prior Art] Conventionally, various kinds of acrylate (meta) derivatives are used for a coating agent, adhesives, etc. which mainly make ink and a coating the start. The epoxy acrylate (acrylic modified epoxy resin) obtained as an example of representation of this (meta) acrylate derivative by the reaction of the bisphenol A diglycidyl ether and the acrylic acid which are shown below is mentioned.

[0003]

[Formula 3]



[0004] By the way, various kinds of applications are presented with the above-mentioned epoxy acrylate as paint for ultraviolet curing (UV coating), although the adhesion which was excellent to the base material has, the paint film is too hard, there is a problem in respect of flexibility, and there is a problem in respect of workability, without the ability also referring to as viscosity low enough moreover.

[0005]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned actual condition, and the purpose is excellent in base material adhesion, and it has flexibility, and is in moreover offering the new (meta) acrylate derivative which is hypoviscosity, and its manufacture approach.

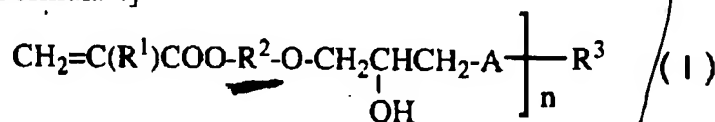
[0006]

[Means for Solving the Problem] As a result of repeating various examination, with the acrylate derivative obtained from the glycidyl alkyl (meta) acrylate of specific structure (meta), this invention persons acquired knowledge that the above-mentioned purpose can be attained easily, and resulted in completion of this invention.

[0007] That is, the 1st summary of this invention consists in the acrylate derivative characterized by what is expressed with the following general formula (I) (meta).

[0008]

[Formula 4]

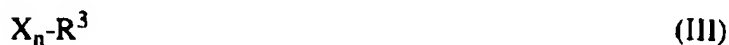
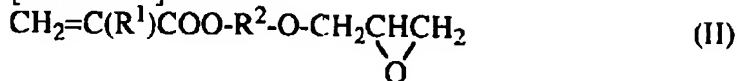


(R¹ the alkylene group of the shape of a straight chain of carbon numbers 4-10, and the letter of branching, and A for a hydrogen atom or a methyl group, and R² among a general formula (I)) - OOC-, -O-, -S-, -N (CH₂CH(OH) CH₂-O-R²-OOC-(R¹) C=CH₂), - N(R⁴)-, -N(CH₂CH(OH) CH₂-O-R²-OOC-(R¹) C=CH₂) OC-, - the residue except the divalent connection radical chosen from the group of N(R⁴) OC- and the active hydrogen content functional group of the compound with which R³ has an active hydrogen content functional group, and n express the integer of 1-4, and above R⁴ expresses the same radical as the above-mentioned residue.

[0009] The 2nd summary of this invention consists in the acrylate derivative characterized by being a reactant with the compound which has the active hydrogen content functional group expressed with the glycidyl alkyl (meta) acrylate expressed with the following general formula (II), and the following general formula (III) (meta).

[0010]

[Formula 5]



(Active hydrogen content functional group as which the meaning of R¹-R³ and n of a general formula (II) and (III) inside is synonymous in a general formula (I), and X is chosen from the group of a carboxyl group, a hydroxyl group, a thiol group, the 1st class amino group, the 2nd class amino group, and an amide group.)

[0011] And the 3rd summary of this invention consists in the manufacture approach of the acrylate derivative characterized by making the compound which has the active hydrogen content functional group expressed with the glycidyl alkyl (meta) acrylate expressed with the above-mentioned general formula (II), and a general formula (III) react (meta).

[0012]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. Although the acrylate (meta) derivative of this invention is expressed with said general formula (I), the greatest structural description is in the alkylene group of R², i.e., the shape of a straight chain of carbon numbers 4-10, or the letter of branching. By having the alkylene group of this specific carbon number, the acrylate (meta) derivative of this invention does not spoil the base material adhesion which was conventionally excellent in the well-known (meta) acrylate derivative, has flexibility, and demonstrates the outstanding property which is hypoviscosity.

[0013] The acrylate (meta) derivative of this invention can also be specified as a reactant with the compound which has the active hydrogen content radical expressed with the glycidyl alkyl (meta) acrylate expressed with the aforementioned general formula (II), and a general formula (III). And the glycidyl alkyl (meta) acrylate expressed with the aforementioned general formula (II) is a compound which epichlorohydrin is made to react to the hydroxyalkyl (meta) acrylate guided from the both-ends diol and the AKURI (meta) acid of carbon numbers 4-10, and is obtained.

[0014] Therefore, about the example of R² (alkylene group of carbon numbers 4-10) in a general formula (I), if the glycidyl alkyl (meta) acrylate of a raw material of explanation expressed with a general formula (II) for convenience shows 4-hydroxy butyl acrylate glycidyl ether, 5-hydroxy pentyl acrylate glycidyl ether, 6-hydroxy hexyl acrylate glycidyl ether, 7-hydroxy heptyl acrylate glycidyl

ether, 8-hydroxy octyl acrylate glycidyl ether, 9-hydroxy nonyl acrylate glycidyl ether, 10-hydroxy decyl acrylate glycidyl ether, these correspondence methacrylate, etc. are mentioned. Desirable R2 in a general formula (I) is the alkylene group of carbon numbers 4-6.

[0015] A in a general formula (I) -OOC- , -O- , -S- , $\text{-N(CH}_2\text{CH(OH)CH}_2\text{-O-R}_2\text{-OOC-(R}_1\text{)C=CH}_2\text{)}$, $\text{-N(R}_4\text{)-}$, $\text{-N(CH}_2\text{CH(OH)CH}_2\text{-O-R}_2\text{-OOC-(R}_1\text{)C=CH}_2\text{)OC-}$, - Express the divalent connection radical chosen from the group of N(R4) OC-, R3 expresses the residue (for example, an aliphatic series saturation hydrocarbon group, an aromatic hydrocarbon radical, an alicycle group hydrocarbon group, etc.) except the active hydrogen content functional group of the compound which has an active hydrogen content functional group, and n expresses the integer of 1-4. And above R4 expresses the same radical as the above-mentioned residue.

[0016] Then, it will be as follows if the compound which has the active hydrogen content functional group of the raw material expressed with a general formula (III) about the example of A (and above R4), R3, and n in a general formula (I) shows to above every connection radical A.

[0017] -OOC- : As a carboxylic-acid > carboxylic acid, - phenyl benzoate dicarboxylic acid, and oleic acid, octylic acid, stearic acid, acrylic-acid, maleic-acid, phthalic-acid, tetrahydrophthalic acid, hexahydrophthalic acid, hydrogenation dimer acid, trimellitic acid, adipic-acid, terephthalic-acid, dimer acid, isophthalic acid, 4, and 4'-benzanilide dicarboxylic acid, 4, and 4'4, 4'-stilbene dicarboxylic acid, 3-carboxy adipic acid, etc. are mentioned, for example.

[0018] -O- : as alcoholic > alcohol For example, ethylene glycol, propylene glycol, a polyethylene glycol, A polytetramethylene glycol, 1,4-butanediol, 1,6-hexanediol, Neopentyl glycol, tricyclodecanedimethylol, 1, 4-dimethylol cyclohexane, Benzene -1, 4-dimethylol, bisphenol A, the bisphenol A poly ethoxy diol, The bisphenol A poly propoxy diol, Bisphenol F, bisphenol F poly ethoxy diol, Bisphenol F poly propoxy diol, trimethylol propane, Trimethylol propane poly ethoxy polyol, trimethylol propane poly propoxy triol, Pentaerythritol PORIETOKISHI tetra-oar, ditrimethylol propane tetra-oar, Ditrimethylol propane PORIETOKISHI polyol, ditrimethylol propane polypropylene POKISHITETORAORU, tris (2-hydroxyethyl) isocyanurate, etc. are mentioned.

[0019] -S- : As a thiol > thiol, - propylidene dithiol, 1, 4-cyclohexane dithiol, 1, 6-hexane dithiol, and 1, 4-benzene dithiol, 1, 3-benzenethiol, 4, and 4'2, 2'-dimercapto diethylether, 1, a 2-dimercapto propane, tris (mercapto phenyl) methane, trimethylol propane TORICHIO glycolate, pentaerythritol hexa thioglycolate, polysulfide, etc. are mentioned, for example.

[0020] $\text{-N(CH}_2\text{CH(OH)CH}_2\text{-O-R}_2\text{-OOC-(R}_1\text{)C=CH}_2\text{)}$: as primary amine > primary amine For example, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, Iminobis pentamine, iminobis propylamine, bis(hexamethylene) triamine, 1, 3, 6-tris aminomethyl hexane, polymethylene diamine, A trimethyl hexamethylenediamine, a MENSENJI amine, isophorone diamine, Bis(4-amino-3-methylcyclohexyl) methane, meta-xylidene diamine, a meta-phenylenediamine, diamino diphenylmethane, diamino diphenyl SURUPON, etc. are mentioned.

[0021] $\text{-N(R}_4\text{)-}$: As secondary amine > secondary amine, a piperidine etc. is mentioned, for example.

[0022] $\text{-N(CH}_2\text{CH(OH)CH}_2\text{-O-R}_2\text{-OOC-(R}_1\text{)C=CH}_2\text{)OC-}$: As an amide of the amide > primary amine of primary amine, an erucic-acid amide, oleic amide, octadecanamide, a BEFENIN acid amide, a 4-sulfonamide-N-phenyl benzamide, a 4-sulfonamide-N-phenyl-4'-chloro benzamide, a 4-amino-N-phenyl benzamide, a dimer acid origin polyamide, etc. are mentioned, for example.

[0023] $\text{-N(R}_4\text{)OC-}$: As an amide of the amide > secondary amine of secondary amine, ethylene screw octadecanamide, ethylene screw oleic amide, an ethylene screw erucic-acid amide, m-xylidene screw octadecanamide, p-phenylene screw octadecanamide, etc. are mentioned, for example.

[0024] The acrylate (meta) derivative of this invention is manufactured by making the compound which has the active hydrogen content functional group expressed with the glycidyl alkyl (meta) acrylate expressed with the aforementioned general formula (II), and said general formula (III) react. Under the present circumstances, let the operating rate of glycidyl alkyl (meta) acrylate and the compound which has an active hydrogen content functional group be the mole ratio which serves as the abbreviation equivalent in the relation between the former epoxy group and the latter active hydrogen (integer of the arbitration per [1-4] molecule). Moreover, a reaction is usually performed under a 100-150-degree C

condition to the bottom of existence of inert solvents, such as toluene, for 2 to 5 hours. Under the present circumstances, according to the class of compound which has the active hydrogen content functional group expressed with said general formula (III) as a reaction catalyst, various kinds of well-known catalysts are used.

[0025] The acrylate (meta) derivative of this invention is independent, or is used for a coating agent, adhesives, etc. which mainly make ink and a coating the start as a constituent with other UV hardenability monomers. As a UV hardenability monomer of above others, for example, ethylhexyl (meta) acrylate, Nonyl phenol ethyleneoxide denaturation (meta) acrylate, an N-vinyl-2-pyrrolidone, Acryloyl morpholine, iso BONIRU (meta) acrylate, 2-hydroxy-3-phenoxy propyl (meta) acrylate, Phthalic-acid mono-DOROKISHI ethyl (meta) acrylate, an acrylic-acid dimer, Bisphenol A ethyleneoxide denaturation di(meth)acrylate, Bisphenol F ethyleneoxide denaturation di(meth)acrylate, Tori propyleneglycol di(meth) acrylate, Pori propyleneglycol di(meth) acrylate, Pori ethylene glycol di (metha)acrylate, hydronalium KISHIBI valine acid neopentyl glycol di(metha)acrylate, Tricyclodecane JIMETANORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, Pen. TAERISURITORUTORI (meta) acrylate, trimethylol propane ethyleneoxide denaturation Tori (meta) acrylate, Trimethylol propane propylene oxide denaturation Tori (meta) acrylate, dipentaerythritol hexa (meta) acrylate, ditrimethylol propane tetrapod (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, etc. are mentioned. These are used in the amount of the range which does not spoil the effectiveness of the metaacrylate derivative of this invention.

[0026]

[Example] 4-hydroxy butyl acrylate glycidyl ether 400g (two mols), 166g [of phthalic acids] (one mol), and triethylamine (catalyst) 1g and p-methoxy phenol (polymerization inhibitor) 300mg were extracted in 1l. 4 opening flask equipped with example 1 thermometer, a cooling pipe, and stirring equipment. And in response to [for about 10 hours] the bottom of a churning condition, epoxy acrylate (A) was obtained at 100 degrees C.

[0027] In the same flask as example of comparison 1 example 1, 144g [of acrylic acids] (two mols) and diglycidyl phthalate 278g (one mol), triethylamine (catalyst) 1g, and p-methoxy phenol (polymerization inhibitor) 200mg were extracted. And in response to [for about 10 hours] the bottom of a churning condition, epoxy acrylate (B) was obtained at 100 degrees C.

[0028] Each following trial was performed about each above-mentioned epoxy acrylate (A) and (B). A result is shown in the below-mentioned table 1.

[0029] (1) Viscosity of epoxy acrylate : the Brookfield viscometer ("BH mold" by Tokyo Keiki Co., Ltd.) was used, and it measured at 25 degrees C.

[0030] Flexibility trial (based on JIS K5400) : (2) Blend the photopolymerization initiator ("IRGACURE 184" by Ciba-Geigy) 3 weight section with the epoxy acrylate 100 weight section. After applying to the thickness of 200 micrometers by the applicator on a hard-glass plate, it lays on 1m conveyor for /in rate, and a high pressure mercury vapor lamp (80 W/cm) is irradiated from the distance of 15cm, a trial film is created until a surface tuck is lost, and the flexibility of the trial film concerned is examined.

[0031]

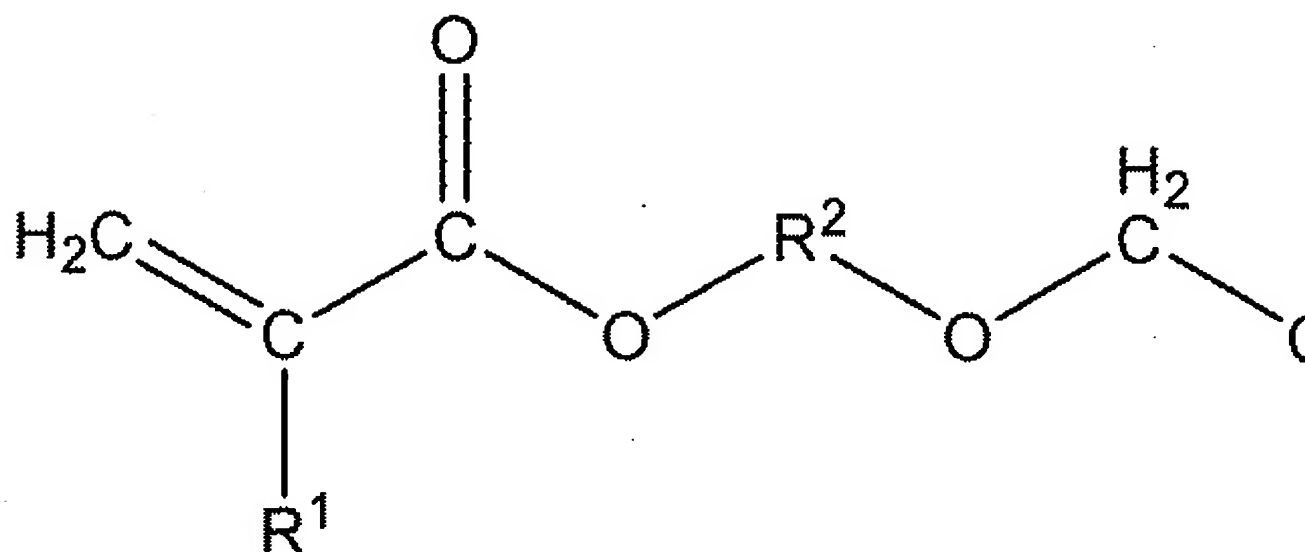
[Table 1]

	25℃粘度	屈曲性
実施例1 エポキシアクリレート (A)	3000 P	200mm
比較例1 エポキシアクリレート (B)	常温固体	折り割れにより測定不能

[0032]

[Effect of the Invention] According to this invention explained above, it excels in base material adhesion, and has flexibility, moreover the new (meta) acrylate derivative which is hypoviscosity, and its manufacture approach are offered, and the place which contributes the acrylate (meta) derivative of this invention to the field of the coating agent which makes ink and a coating the start, or adhesives is size.

[Translation done.]



$R^1 = \text{H, Me}$

$R^2 =$ 炭素数2～10の直鎖状または分岐状のア

